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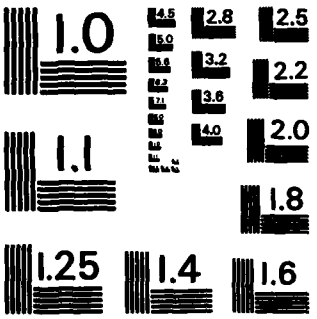

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The rates and mechanisms through which the electronically excited states of oxygen are formed and destroyed in the upper atmosphere have been studied in a discharge flow system. Using a technique in which excited states are formed by surface catalyzed recombination, rate constants have been obtained for the quenching of the O2(A), O2(c) and O(singlet S) states by atmospheric species. The yields of the electronically excited states O2(singlet delta), O2(singlet sigma) and O(singlet S) in atom recombination have been determined directly. Evidence has been found for the existence of a precursor in each of these systems. The rate laws for the formation of O2(A), O2(c) and O(singlet S) have been established and rate constants for some of the elementary steps have been determined by combining these rate laws with the results of quenching experiments. Final report, AFOSR-79-0088, Electronically Excited Oxygen.

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FINAL REPORT

ELECTRONICALLY EXCITED ATOMIC AND MOLECULAR OXYGEN

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1 March 1979 - 30 June 1984

Final Report
Research Project 79-0088
Electronically Excited Atomic and Molecular Oxygen

Objectives:

The natural phenomenon whose understanding motivated this study is the night airglow . The objective of our study was the identification of the mechanism by which the observed emission from O_2 and O are excited at an altitude of about 100 km in the atmosphere of Earth and Venus.

On a more fundamental level our objective was to determine the rate and mechanism by which the recombination of oxygen atoms produces the electronically excited states of oxygen molecules and atoms.

Status of Research Effort:

The experiments undertaken in this project can be divided into two series. The first series of experiments attempted to produce a sudden high concentration of electronically excited oxygen by the surface catalyzed recombination of oxygen atoms on a nickel surface. These experiments were an attempt to determine the quenching and other relaxation processes of $O_2(A^3\Sigma u^+)$, $O_2(A'^3\Delta u)$,& $O_2(c^1\Sigma u^-)$ which have not previously been determined. The second series attempted to determine the rate laws governing the formation of electronically excited states of O_2 in the recombination of oxygen atoms. The results of these experiments could then be combined with those from series 1 to calculate the absolute yield of each excited state in the recombination process.

Surface Catalyzed Recombination Studies

Attempts to produce an instantaneous concentrate of $O_2(A)$, $O_2(A')$, $O_2(c)$, and $O(^1S)$ met with success and rate constants for the quenching of these species by a number of gases were determined. These were reported in a series of papers (1,2,3,4,5) and are summarized in Table 1. Attempts to

TABLE 1: Rate constants for quenching of $O_2(A_3\Sigma_u^+)$, $O_2(A'^3\Delta u)$ and $O_2(c'\Sigma_u)$ by various gases

Quenching series	$O_2(A^3\Sigma_u^+)$ and $O_2(A'^3\Delta_u)$	$O_2(c^1\Sigma_u^-)$	$O(^1S)$
$O(^3P)$	$(1.29\pm0.1)\times10^{-11}$[c,d]	$(5.9\pm0.6)\times10^{-12}$	
$O_2(a^1\Delta g)$	$(8.1\pm1.6)\times10^{-11}$	$(6.0\pm2.4)\times10^{-12}$	2×10^{-10}
O_2	1.3×10^{-13}	3×10^{-14}	
CO_2	7×10^{-13}	$<6\times19^{-14}$	
SF_6	6×10^{-13}	2×10^{-13}	
N_2O	1.8×10^{-12}	4×10^{-13}	
He		6×10^{-15}	
Ar	7.2×10^{-16}	6×10^{-16}	

[c] All units are cm^3 $molecule^{-1}$ s^{-1}

[d] Indicated error limits are the 1σ statistical uncertainties.

determine the temperature dependencies of these quenching processes were less successful. The only process for which we obtained data is the reaction:

$$O_2(A) + O \longrightarrow \text{quenched products}$$

Assuming that the temperature dependence can be represented by the Arrhenius equation we have plotted ln k_1 versus 1/T in Figure 1.

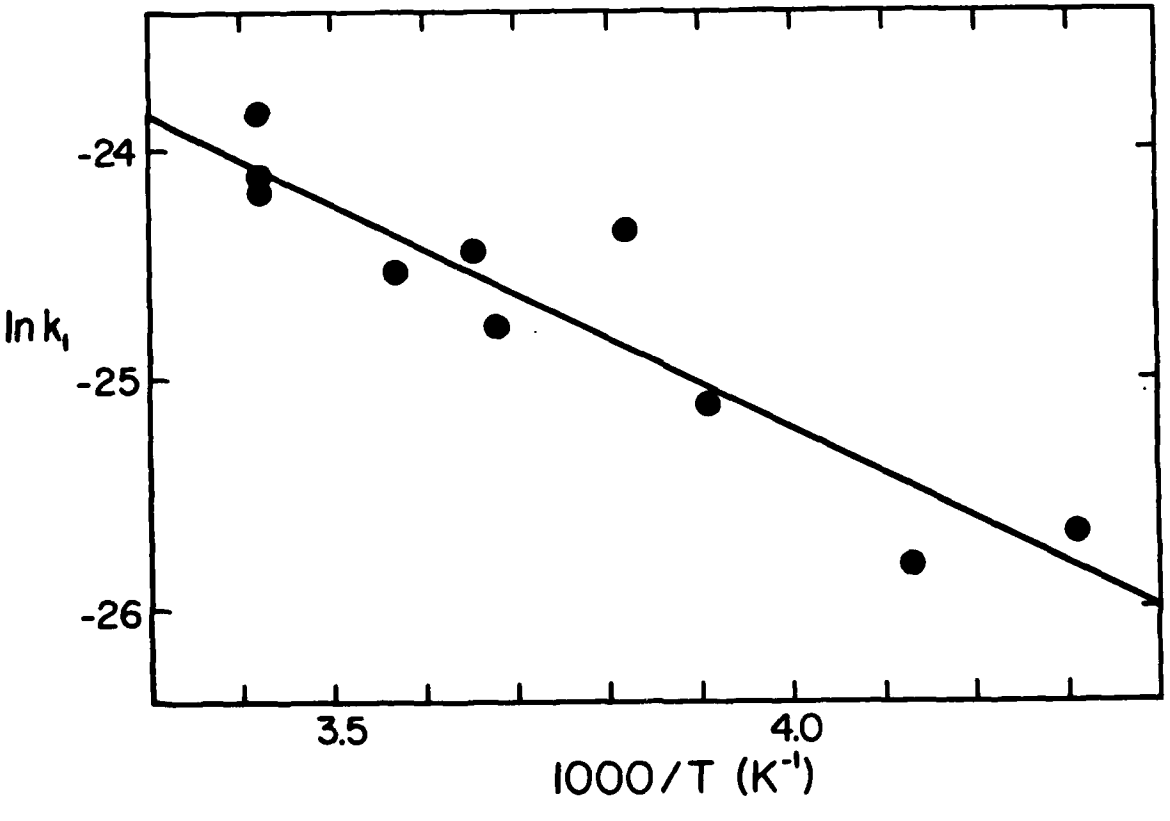

Fig 1

The line drawn through these points yields:

$$k_1 = 2.9 \times 10^{-8} e^{-(1965/T)} cm^3 molec^{-1} s^{-1} \quad (2)$$

Although k_1 was determined specifically for only the second vibrational level of the $O_2(A)$ state we have reason to believe that it is not significantly different for any level which is formed on the nickel surface (v' = 0 to 5). Not only are the quenching rate constants for other levels insignificantly different but the distribution in these vibrational levels does not appear to change significantly with changing temperature.

The primary purpose of these experiments was to determine whether in the Earth's night airglow the quenching of the $O_2(A)$ state by oxygen atoms is significant. Unfortunatley the lowest temperature at which we could conduct our experiments was 232K. However, if we assume that the temperature dependence represented by equation 2 can be extended another 32°, then $k_1(200K) = 1.5 \times 10^{-12} cm^3 molec^{-1} s^{-1}$. This is a factor of 20 smaller than the room temperature value. In the upper atmosphere where the peak oxygen atom concentration is 6.5×10^{-11} atoms cm^3, the rate at which $O_2(A)$ is quenched by O is about an order of magnitude smaller than the radiative decay rate ($0.2s^{-1}$). We conclude, therefore, that oxygen atoms are not very important quenchers of the $O_2(A)$ state in the upper atmosphere.

The magnitude of the preexponential in equation 2 calls for some comment. It is about two orders of magnitude greater than normal (i.e. that associated with gas kinetic collision frequency). Therefore it may not be

wise to assume that the temperature dependence of this rate constant is well represented by equation 2 much beyond the temperature range of these measurements, especially at high temperatures. This reservation does not affect our qualitative conclusion that oxygen atoms do not dominate the $O_2(A)$ removal rate in the upper atmosphere, since this would hold true even if the rate constant at 200K is no smaller than the value which we measured at 232K.

The measurement of rate constants for a series of vibrational levels of these excited states has not been possible except for the quenching of $O_2(A)$ by oxygen atoms where values were determined for the 5 lowest vibrational levels. These are summarized in Figure 2.

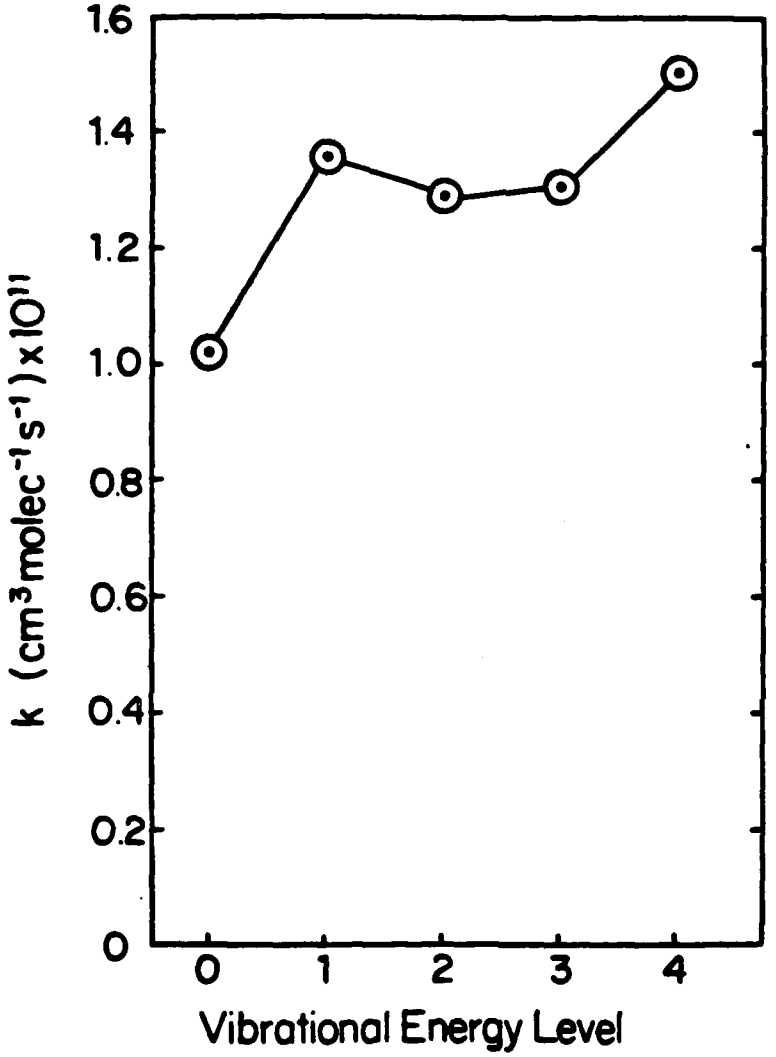

Fig. 2

Atom Recombination Studies

In these experiments the kinetic dependence of the emissions from the various excited states of oxygen that result from atom recombination were determined

1. Emission for $O(^1S)$ was found to obey the following rate law (6)

$$I = k[O]^2[M]/[O_2(a^1\Delta g)]$$

where $k = 2.7 \times 10^{-27}$ $cm^3 molec^{-1}$ s^{-1}. This rate law is consistent only with a "Barth Type" mechanism given by equations [1-5], where reaction [4] occurs at collision frequency 5×10^{-10} $cm^3 molec^{-1}$ s^{-1} and k_1 is at least 25% of the total recombination rate constant ($4.75 \times 10^{-31} cm^6 molec^{-2}$ s^{-1}).

$$O + O + M \rightarrow O_2^* + M \qquad [1]$$

$$O_2^* + O \rightarrow O_2 + O(^1s) \qquad [2]$$

$$O_2^* + O \rightarrow \text{all products} \qquad [3]$$

$$O(^1S) + O_2(^1\Delta g) \rightarrow \text{quenched products} \qquad [4]$$

$$O(^1S) \rightarrow O(^1D) + h\nu(557.7\ nm) \qquad [5]$$

2. Emissions from $O_2(A^3\Sigma u^+)$ and $O_2(A'^3\Delta u)$ were found to obey the rate law (7)

$$I = k[O]^2[M]/[O_2]$$

which is consistent with the simple mechanism given by reactions [6-8].

$$O + O + M \rightarrow O_2(A) + M \qquad [6]$$

$$O_2(A) + O_2 \rightarrow \text{quenched products} \quad [7]$$

$$O_2(A) \rightarrow O_2(X) = h\nu(\text{Herzberg I bands}) \quad [8]$$

Combining these measurements with the quenching data provided by the surface catalyzed experiments yields a value for k_6 which is still almost an order of magnitude too small to explain the night airglow emission intensity from $O_2(A)$.

Emission form $O_2(c^1\Sigma u^-)$ was found to obey the rate law (7)

$$I = [O][M]^2/[O_2]$$

Such a kinetic dependence suggests the presence of a precursor (O_2^*) involved in the process as described by reactions [9-13].

$$O + O + M \rightarrow O_2^* + M \quad [9]$$

$$O_2^* + O_2 \rightarrow \text{quenched products} \quad [10]$$

$$O_2^* + M \rightarrow O_2(c) + M \quad [11]$$

$$O_2(c) + O \rightarrow \text{quenched products} \quad [12]$$

$$O_2(c) \rightarrow O_2(X) + h\nu(\text{Herzberg II bands}) \quad [13]$$

Quantum yields in these reactions have yet to be measured in the laboratory.

3. Emission from $O_2(b\ ^1\Sigma g^+)$ was found to have a complex kinetic dependence because of the unique involvement of ground state O_2 (8). Steady state and

time dependent measurements required the presence of a precursor (O_2^*) as indicated in the mechanism described by reactions [14-18]:

$$O + O + M \rightarrow O_2^* + M \qquad [14]$$

$$O_2^* + O \rightarrow \text{quenched products} \qquad [15]$$

$$O_2^* + O_2 \rightarrow O_2(b) + O_2 \qquad [16]$$

$$O_2^* + O_2 \rightarrow \text{all products} \qquad [17]$$

$$O_2(b) \rightarrow O_2(X) + h\nu(762\ nm) \qquad [18]$$

where O_2^* remains unidentified but $k_{15}/k_{17} = 2.6$ and $k_{14} > 1.6 \times 10^{34}$ $cm^6 molec^{-2} s^{-1}$.

4. Emission from $O_2(a\ ^1\Delta g)$ was found to have a complex kinetic dependence on molecular oxygen very similar to that observed for $O_2(b)$. The effect of adding molecular oxygen to a stream of oxygen atoms is shown in Figure 3.

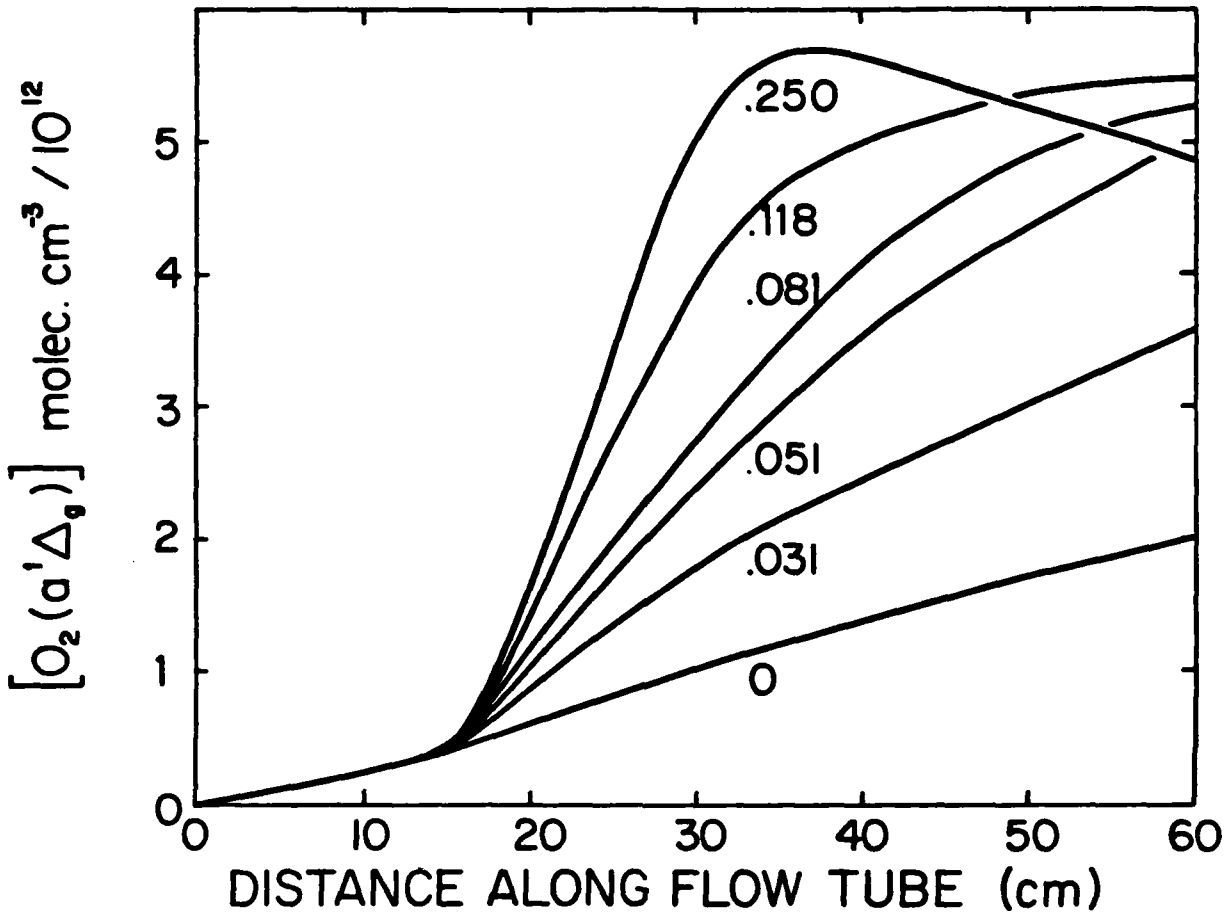

FIGURE 3
The growth of $O_2(a)$ from atom recombination along a flow tube (time/cm = 6.4 x 10^{-3}s). The numbers next to each curve give the pressure of O_2 (in torr) added at the "15-cm position."

The rate constant in the absence of O_2 is less than 10% of the rate constant for total recombination. With O_2 present it rises by almost a factor of 10. The detailed kinetic analysis remains to be completed.

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Publications Resulting from This Project

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2. "Deactivation of $O_2(A^3\Sigma u^+)$ by O_2, O and Ar", R.D. Kenner and E.A. Ogryzlo, Int. J. Chem. Kin., 7, 501 (1980).
3. "Excitation of the Green Line in the Night Airglow", R.D. Kenner, E.A. Ogryzlo and P.T. Wassell, Nature, 291, 398 (1981).
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7. "Orange Chemiluminescence from Nitrogen Dioxide", R.D. Kenner and E.A. Ogryzlo, J. Chem. Phys., 80, 1 (1984).
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Professional Personnel Associated with Research Effort

Dr. R.D. Kenner (Post Doctoral Associate)

Dr. P.T. Wassell (Graduate student and Post Doctoral Fellow), Ph.D. 1981.

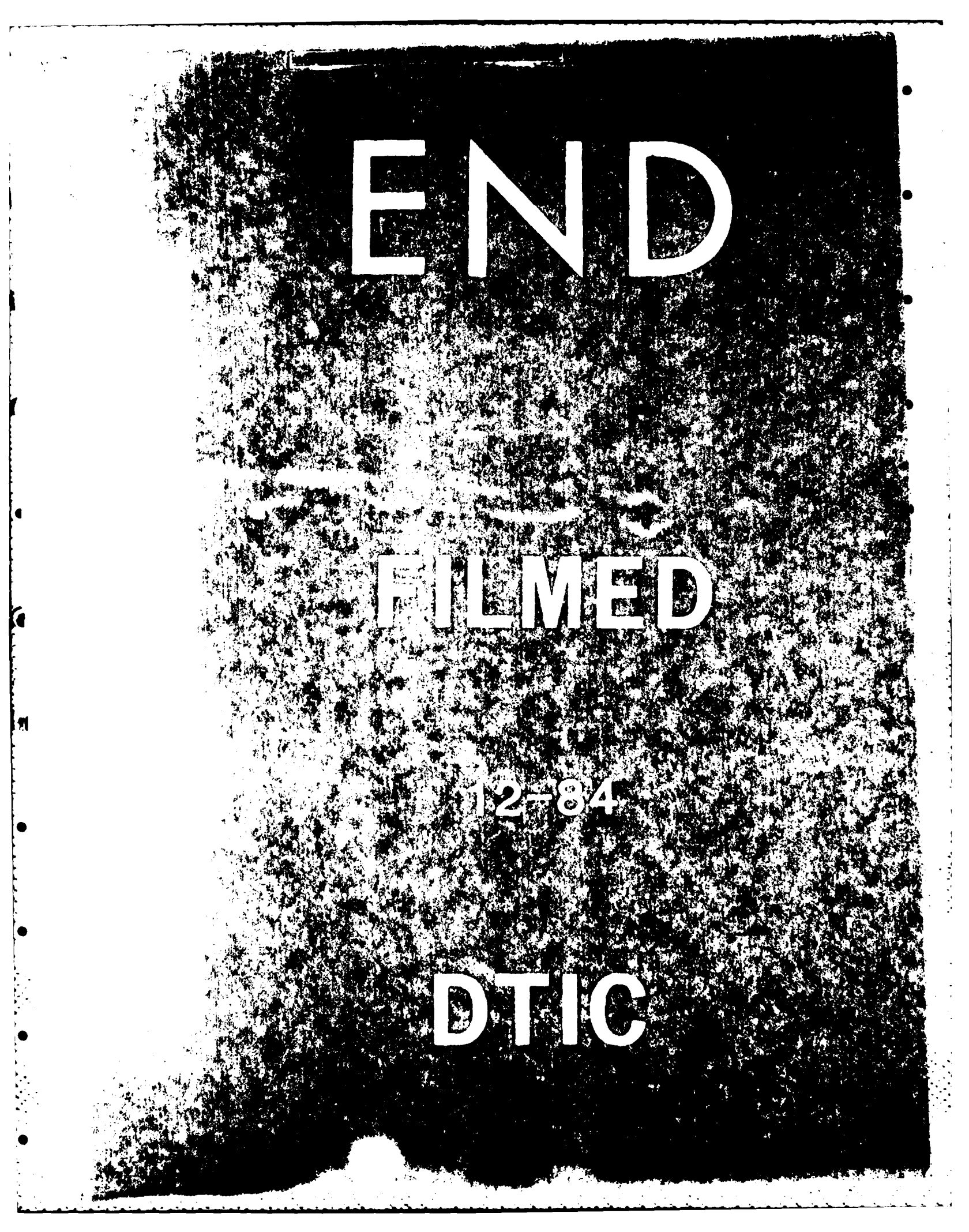
Interactions

Invited paper to be presented at the PAC conference, Honolulu, December 18, 1984. E.A. Ogryzlo, Y.Q. Shen and P.T. Wassel, "The yield of $O_2(a\ ^1\Delta g)$ in Atom Recombination".

Invited Paper to be presented at I.G.U. Conference, San Francisco, December 2, 1984, E.A. Ogryzlo, "Laboratory Studies of the Excitation of O_2 in Atom Recombinations".

Invited Paper presented at the A.C.S. Conference, Philadelphia, August 24, 1984, E.A. Ogryzlo, "Chemiluminescence Association Reactions in the Upper Atmosphere".

Invited Paper presented at COSMO-84, Tampa, January 4, 1984, E.A. Ogryzlo, Y.Q. Shen and P.T. Wassel, "The Yield of $O_2(b\ ^1\Sigma g^+)$ in Oxygen Atom Recombination".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